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TITLE: ORGANIC ELECTROLYTE

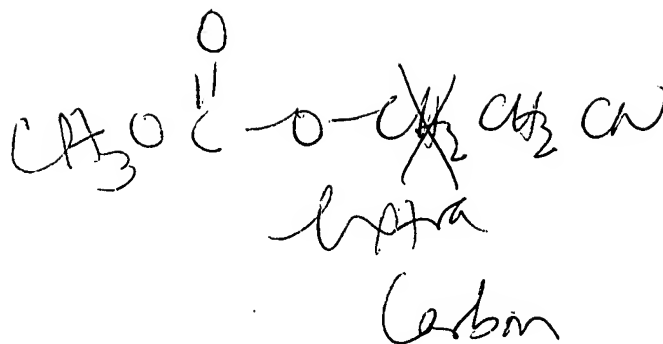
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ABSTRACT:

PROBLEM TO BE SOLVED: To improve dielectric constant, lower freezing point, increase boiling point, improve ion conductivity, by including at least one kind of nitril compounds as solvent of electrolyte salt.

SOLUTION: Nitril compound contained in solvent of electrolyte salt is represented by a formula $\text{R1COO}-(\text{CH}_2)_a-\text{CN}$. Where, R1 is hydrogen atom, alkyl group where number of carbons is 1-3, alkoxy group where number of carbons is 1-3, a is an integer of 1-3, preferably 2. As electrolyte salt, preferably, lithium salt is used for a lithium secondary battery, and fourth grade ammonium salt or fourth grade phosphonium salt is used for an electric double layer capacitor or an electrolyte capacitor. Organic electrolyte is constituted by adding the electrolyte salt into this nitril compound, and contents of the electrolyte salt is usually selected in a range of about 0.1-2 mol/dm³.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] In more detail, this invention used the organic electrolytic solution and a specific nitril compound as a solvent of an electrolyte salt, for example, relates to a lithium cell, a lithium ion rechargeable battery, an electric double layer capacitor, an electrolytic capacitor, etc. at the useful organic electrolytic solution.

[0002]

[Description of the Prior Art] The organic electrolytic solution consists of systems which dissolved the electrolyte salt in the organic solvent, and, generally is used as components, such as a lithium cell (primary rechargeable battery), a lithium ion rechargeable battery, an electric double layer capacitor, an electric double layer capacitor, and an electrolytic capacitor. By the way, in order to dissolve an electrolyte salt well and to raise whenever [ionic dissociation / of an electrolyte salt] as requirements for the above-mentioned organic solvent, it is the most fundamental Important that a dielectric constant is high, and in order to make low cell internal pressure under that the congealing point is low in order to raise ion conductivity on it and to secure the ion conductivity at the time of low temperature by hypoviscosity as much as possible, and cell fabrication operation nature and an elevated temperature, to be a high-boiling point etc. is demanded. Moreover, when using for a lithium cell or a lithium ion rechargeable battery, to bear the severe oxidation by the electrode interface by that they are a lithium and nonresponsiveness (aprotic system) and cell voltage being high and a reduction environment etc. is needed.

[0003] however, in practice, many above-mentioned need properties should conflict in molecular structure in many cases, for example, should obtain a high dielectric constant -- obtaining -- then, a high polar molecule -- not becoming -- it does not obtain but is easy to become hyperviscosity as the result. in the present lithium cell and a lithium ion rechargeable battery, two sorts, ethylene carbonate (abbreviated name: display like EC and the following) and propylene carbonate (PC), are used as a solvent (the main solvent is called hereafter) of a high dielectric constant -- **** -- it does not pass but there are the following problems.

[0004] Since EC is a solid-state (congealing point: 37 degrees C) below in ordinary temperature, if the congealing point is not reduced, it cannot be used by using together with PC (congealing point: -49 degrees C) or other aprotic system solvents (the solvent except PC being called an assistant solvent the following) of the low congealing point. As an assistant solvent, dimethyl carbonate (congealing point: display like 3 degrees C, abbreviated-name: DMC, and the following), Diethyl carbonate (freezing point: -43 degrees C, DEC), 1, 2-dimethoxyethane (freezing point: -58 degrees C) Although DME etc. is used and the viscosity of these assistant solvent is low, a dielectric constant is also low (DMC:3.1, DEC:2.8, DME:7.2), and the boiling point is also low (DMC:90 degree C, DEC:127 degree C, DME:85 degree C). The congealing point of the electrolytic solution is [at most]. -Although it is needed that it is [10 degrees C or less] -20 degrees C or less preferably, and it is considered and designed to the congealing-point fall effectiveness by the dissolution of an electrolyte salt since it is this congealing-point fall, about at least 30 - 40 % of the weight is required for the amount of PC used together or an assistant solvent among [all] a solvent, and it is very difficult to make it fewer than this. It is the present condition to reduce the boiling point (238 degrees C) of EC sharply as a result according to concomitant use of an assistant solvent, although a dielectric constant falls, and conductivity does not necessarily fall to coincidence by the viscosity down (however, conductivity will fall if the amount of assistant solvents increases too much). Therefore, it looks forward to the new main solvent with the low congealing point.

[0005] On the other hand, although there is no problem [like EC / in / a freezing point is low (-49 degrees C), and / unlike EC / the above] whose PC is, since the graphite system carbon ingredient used for a negative electrode receives decomposition when it uses for a lithium ion rechargeable battery, it cannot be used other than the cell which used the carbon ingredient of an amorphous system for the negative electrode. However, the cell which used the amorphous

system carbon ingredient has the large degree of the sag produced with discharge (use), and the cell using few graphite system ingredients of whenever [by this discharge (use) / sag] is becoming in use recently. However, if it becomes the main solvent which can apply this amorphous system carbon ingredient in the present condition, EC of an ordinary temperature solid-state will be in the condition of only.

[0006]

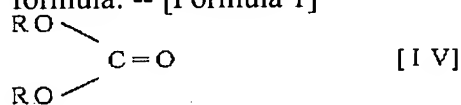
[Means for Solving the Problem] In addition to the high dielectric constant which is a need property as a main solvent, this invention persons have the high boiling point at the low congealing point. The place which advanced research wholeheartedly about the electrolytic-solution solvent possessing terms and conditions, like ion conductivity is excellent, It came to complete a header and this invention for the nitril compound of a low-grade aliphatic series carboxylate system or a carbonate system making above-mentioned EC and the fault of PC cancel entirely, and being able to use it also as the new main solvent of the expected purpose, or an assistant solvent.

[0007] That is, this invention is formula: $R1-COO-(CH_2)_a-CN$ as a solvent of an electrolyte salt. The organic electrolytic solution characterized by including at least one sort of the nitril compound [I] shown by [I] (a hydrogen atom, the alkyl group of carbon numbers 1-3 or alkoxy group [of carbon numbers 1-3];, and a of the inside of a formula and R1 are the integers of 1-3) is offered.

[0008] The above-mentioned nitril compound [I] can be manufactured according to the procedure which it is divided roughly into the two following groups a and b, and is shown below.

Low-grade aliphatic series carboxylate system type : a) $R1'-COOH$ Low-grade aliphatic carboxylic acid of [II] (inside of formula and $R1'$ is a hydrogen atom or the alkyl group of carbon numbers 1-3). () A formic acid, an acetic acid, a propionic acid, n-butanoic acid, an isobutyric acid [II] or its acid anhydride, an acid chloride, or ester (methyl formate, methyl acetate, methyl propionate, etc.) Namely, formula: $HO-(CH_2)_a-CN$ By making it react with the cyano alcohol (2-cyano ethanol, 3-cyano propanol, etc.) [III] of [III] (the inside of a formula and a are the above and this meaning) (esterification or ester interchange), formula: $R1'-COO-(CH_2)_a-CN$ The cyano methyl of the nitril compound shown by [Ia] (the inside of a formula, $R1'$, and a are the above and this meaning) [Ia], i.e., a formic acid, an acetic acid, a propionic acid, and n-butanoic acid, 2-cyano ethyl, 3-cyano propyl ester, etc. are obtained.

[0009] The KUROROGI acid alkyl of $ClCOOR$ (the inside of a formula and R are methyl, ethyl, n-propyl, or isopropyl) by making it react with the above-mentioned cyano alcohol [III] Carbonate system type : b) Formula: $RO-COO-(CH_2)_a-CN$ The unsymmetrical carbonate system nitril compound of the nitril compound of [Ib] (the inside of a formula, and R and a are the above and this meaning) [Ib], i.e., methyl carbonate, ethyl carbonate, carbonic acid n-propyl, carbonic acid isopropyl cyano methyl, 2-cyano ethyl, and 3-cyano propyl is obtained. as an exception method -- formula: -- [Formula 1]



A nitril compound [Ib] is obtained by carrying out the ester exchange reaction of the carbonic acid dialkyl [IV] of (the inside of a formula and R are the above and this meaning) to the low-grade aliphatic-carboxylic-acid cyano alkyl [V] of above-mentioned cyano alcohol [III] or formula: $R1'-COO-(CH_2)_a-CN$ [V] (the inside of a formula, $R1'$, and a are the above and this meaning). In addition, in the case of this ester interchange method, as an actual industrial manufacturing method, it is dominance, but since carbonic acid dialkyl [IV], and the cyano alcohol [III] or low-grade aliphatic-carboxylic-acid cyano alkyl [V] of a raw material remains as an unreacted object and the carbonic acid screw (cyano alkyl) of the symmetry carries out a byproduction as mixture, fractional distillation purification is needed.

[0010] Thus, if it is in the nitril compound [I] manufactured and the carbon number of R1 (an alkyl group or alkoxy group) or a becomes four or more, the content of a nitrile group (CN) will become low and a dielectric constant required as a main solvent will fall. Moreover, in $a=1-3$, the case of $a=2$ is advantageous practically in respect of manufacture, such as raw material acquisition and synthetic conditions, and cost. although the carbonic acid screw of the symmetry which carries out a byproduction by the exception method of Above b (cyano alkyl), i.e., a carbonic acid screw, (cyano methyl), a carbonic acid screw (2-cyano ethyl), and a carbonic acid screw (3-cyano propyl) are a high dielectric constant since they contain two nitrile groups in a molecule, since [furthermore,] it becomes hyperviscosity remarkably and ion conductivity falls on the contrary -- this invention -- being out of range .

[0011] As the above-mentioned electrolyte salt, for example Perchloric acid, tetrafluoroboric acid, lithium salt; tetra-alkyl quarternary ammonium salt (tetramethylammonium --), such as a hexa full OROHI acid, hexa fluorophosphoric acid, and trifluoro methansulfonic acid the 4th class phosphonium salt (tetramethylphosphonium --) of; tetra-alkyl, such as tetraethylammonium and tetra-n-butyl ammonium Suitable tetraethyl phosphonium, tetra-n-propyl phosphonium, etc. -- etc. -- in these Lithium salt is used in a lithium or the object for lithium ion rechargeable batteries, and

quaternary ammonium salt and the 4th class phosphonium salt are used in an electric double layer capacitor or the object for electrolytic capacitors.

[0012]

[Embodiment of the Invention] What is necessary is for the organic electrolytic solution concerning this invention to consist of systems which blended the electrolyte salt with at least one sort of a nitril compound-[I]. like ****, and just to usually select the content of an electrolyte salt here so that it may become 0.1-2 mols / about three-dm density range. In addition, the application of the organic electrolytic solution obtained according to the class of nitril compound [I] to be used is as follows. It is easy to decompose by a reaction or charge and discharge with lithium salt, and formic-acid cyano alkyl and acetic-acid cyano alkyl ester [Ia] are unsuitable to a lithium cell and a lithium ion rechargeable battery (however, other applications: with [in an electric double layer capacitor or an electrolytic capacitor] no problem). On the other hand, in the case of nitril compounds other than the two above-mentioned sort [I], it was usable satisfactory including the lithium cell or the lithium ion rechargeable battery, and it turned out in it that propionic-acid 2-cyano ethyl ester [Ia], methyl carbonate and 2-cyano ethyl, and ethyl carbonate and 2-cyano ethyl [Ib] have a desirable property in application to a lithium cell and a lithium ion rechargeable battery especially.

[0013] Are in the organic electrolytic solution of this invention, and it adds to the above-mentioned nitril compound [I]. Other polar solvents currently used from the former (the main solvent and assistant solvent), for example, a lithium cell, The ethylene carbonate which is an aprotic system solvent in the object for lithium ion rechargeable batteries, Propylene carbonate, dimethyl carbonate, diethyl carbonate, 1, 2-dimethoxyethane, Gamma-butyrolactone, gamma-valerolactone, dimethyl sulfoxide, A sulfolane, a tetrahydrofuran, 2-methyl tetrahydrofuran, etc.; In an electric double layer capacitor or the object for electrolytic capacitors, it adds to these aprotic system solvent. N-dimethylformamide, N-dimethylacetamide, ethylene glycol, etc. can be used together. 0-3; and c residue; b excluding all the hydroxyl groups from the compound with which, as for R2, alkyl group; R3 of carbon numbers 1-4 have 1-4 hydroxyl groups among a bR3(OCH2CH2CN) c [type Moreover, a formula : (R2O) 1-4 (-- however, the compound shown by] whose b+c is 1 - 4), for example, methyl and 2-cyano ethyl ether, -- Ethyl and 2-cyano ethyl ether, n-propyl and 2-cyano ethyl ether, 2-methoxy ethyl and 2-cyano ethyl ether, An ethylene glycol screw (2-cyano ethyl) Cyano ethyl ether system solvents (high dielectric constant solvent), such as; or the bis(2-cyano ethyl) ether [O(CH2CH2CN) 2 </SUB>], such as the ether, can also be used together (these cyano ethyl ether system quantity dielectric constant solvent). It indicates to JP,10-116514,A. In this case, what is necessary is just to select the amount of a polar solvent besides the above, and/or a cyano ethyl ether system quantity dielectric constant solvent in 5 - 95% of the weight of the range among electrolytic-solution solvent total amounts.

[0014]

[Example] Next, the example of manufacture and an example are given and this invention is explained more concretely.

276.2g [of formic acids] (six mols) and 2-cyano ethanol 355.5g (five mols), cyclohexane 300g, and 6g of concentrated sulfuric acid are taught to 4 opening flask equipped with the example of manufacture 1 (manufacture of formic-acid 2-cyano ethyl ester) water column, and the reflux cooling pipe, and an esterification reaction is performed for 8 hours, carrying out azeotropy removal of the water generated under reflux. Although the reaction advanced at the temperature which is about 65-70 degrees C in order that a lot of water might generate the early stages of a reaction, it reacted further after 2 - 3-hour progress, flowing desiccation nitrogen gas (temperature rises to about 85-90 degrees C). If cool after a reaction, 500ml of pure water and toluene 300ml are added, a sodium-hydroxide water solution is used and it neutralizes and puts, since it will separate into two-layer, after leaving the upper layer, discarding a lower layer (water layer), and 500ml of pure water washing this upper layer 4 times and carrying out reduced pressure distilling off of a cyclohexane and the toluene, it refines by vacuum distillation further and the specified substance is obtained. The specified substance was transparent and colorless hypoviscosity liquid, and was -44 degrees C in a dielectric constant 35.8, 207 degrees C of boiling points, and congealing point.

[0015] In the example 1 of example of example of manufacture 2 (acetic-acid 2-cyano ethyl ester) manufacture 3 (propionic-acid 2-cyano ethyl ester) manufacture, except using an acetic acid or a propionic acid instead of a formic acid, an esterification reaction, is performed on the same conditions and each specified substance is obtained. The description and the characteristic value of each specified substance are as follows.

Example 2 of manufacture Example 3 of manufacture Sex ** Transparent and colorless hypoviscosity liquid
Transparent and colorless hypoviscosity liquid Dielectric constant 18.7 16.7 ** Point 210 degrees C 217 degrees C
Congealing point -32 degrees C -16 degrees C [0016] Teaching beforehand 2-cyano ethanol 142.2g (two mols) which carried out dehydration processing, toluene 300g, and triethylamine 273g (2.7 mols) in molecular-sieve 3A, respectively, and agitating violently under ice-cooling (10 degrees C or less), KUROROGI acid methyl 236.3g (2.5

moles) is gradually dropped at an example of manufacture 4(methyl carbonate and 2-cyano ethyl) 4 opening flask, and is made to react to it over 3 hours. Raise after dropping termination and temperature to 40 degrees C, and it is made to react for further 2 hours, and methanol 32g (one mol) is added, 2 more hour churning is performed, subsequently it cools, 500ml of pure water is added, it puts after churning about 5 minutes, a management is separated, 500ml of pure water washes 4 times, toluene is distilled off, it refines by vacuum distillation further, and the specified substance is obtained. The specified substance was transparent and colorless hypoviscosity liquid, and was -11 degrees C in a dielectric constant 24.6, 85 degrees C (20mmHg) of boiling points, and congealing point.

[0017] After using as the solvent the nitril compound obtained in an example 1 - the examples 1-4 of 4 manufactures and producing the molar solution (electrolytic solution) of a hexa fluorophosphoric acid lithium (LiPF₆), respectively, the conductivity in 1kHz and 20 degrees C was measured using LCZ meter. The result is as follows.

Conductivity Nitril compound (a siemens/cm) 1. formic-acid 2-cyano ethyl 5.8×10^{-3} 2. acetic-acid 2-cyano ethyl 3.1×10^{-3} 3. propionic-acid 2-cyano ethyl 2.5×10^{-3} 4. methyl carbonate and 2-cyano ethyl 8.1×10^{-4}

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1] The organic electrolytic solution characterized by including at least one sort of the nitril compound shown by formula: $R1-COO-(CH_2)_a-CN$ (a hydrogen atom, the alkyl group of carbon numbers 1-3 or alkoxy group [of carbon numbers 1-3];, and a of the inside of a formula and R1 are the integers of 1-3) as a solvent of an electrolyte salt.

[Claim 2] The organic electrolytic solution according to claim 1 whose a is 2 in a nitril compound.

[Claim 3] The nitril compound according to claim 1 a hydrogen atom, methoxy, or whose ethoxy ***** a R1 is 2 in a nitril compound.

[Claim 4] Claim 1 whose electrolyte salt is lithium salt thru/or the organic electrolytic solution of any one publication of three.

[Claim 5] Claim 1 whose electrolyte salts are tetra-alkyl quarternary ammonium salt and/or the 4th class phosphonium salt of tetra-alkyl thru/or the organic electrolytic solution of any one publication of three.

[Claim 6] Claim 1 which uses other solvents together to a nitril compound thru/or the organic electrolytic solution of any one publication of five.

[Translation done.]